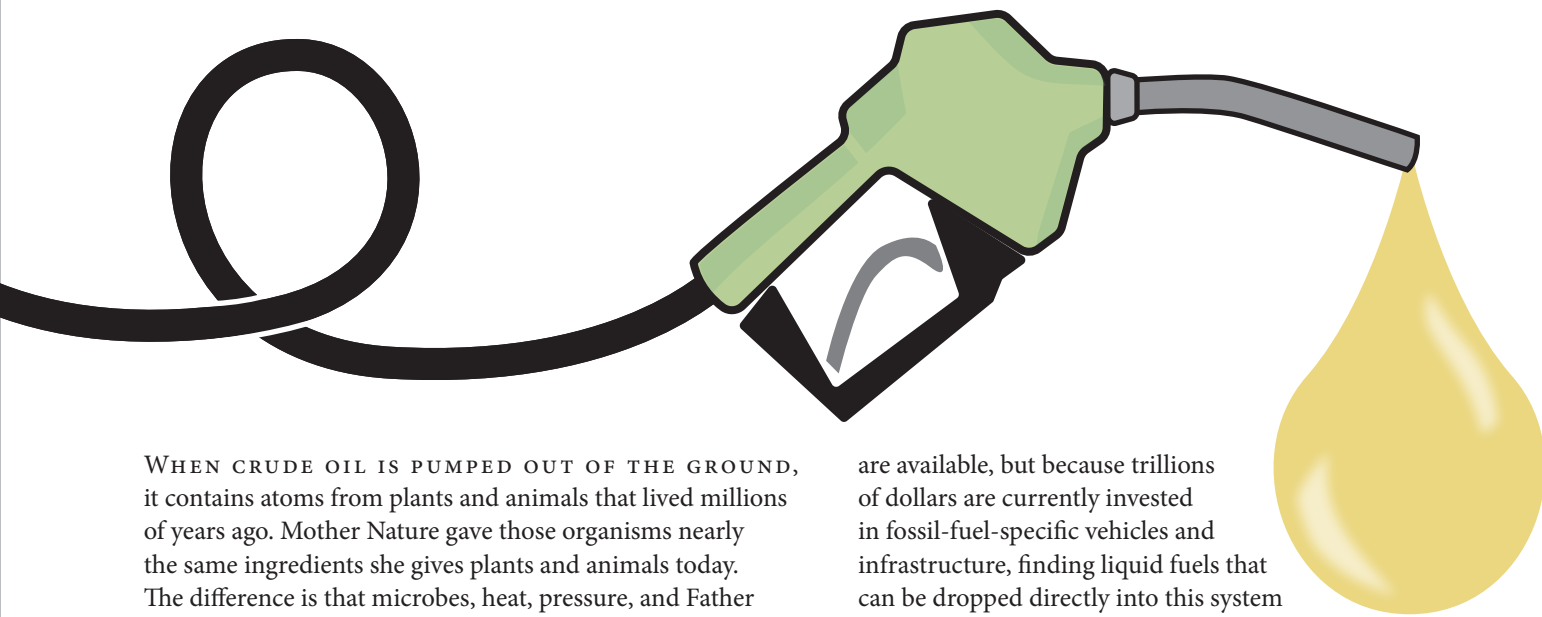


BREAKING THE BOND

CAN CHEMISTRY HELP UNBIND US FROM FOSSIL FUELS?



WHEN CRUDE OIL IS PUMPED OUT OF THE GROUND, it contains atoms from plants and animals that lived millions of years ago. Mother Nature gave those organisms nearly the same ingredients she gives plants and animals today. The difference is that microbes, heat, pressure, and Father Time have done all the work to dismantle the complex living things into simpler molecules that are now used to produce energy. To make similar fuels directly from plant matter today, scientists—including some at Los Alamos—have developed multiple approaches to do the dismantling themselves.

The simple molecules in crude oil are mostly long chains of carbon and hydrogen atoms aptly called hydrocarbons. Hydrocarbons are suitable for making fuel because they are energy dense, meaning that a small volume can produce a large amount of energy. Fossil fuels, such as oil, coal, and natural gas, are found all over the world, and although they require refining after extraction, this processing is fairly straightforward and is now well established, making the fuel relatively inexpensive to buy.

Until recent decades, however, multiple impacts of fossil fuels were largely ignored. First, there is damage to the environment: releasing previously buried carbon into the atmosphere dramatically alters the climate, with grave consequences for life on Earth. Second, importing oil from foreign countries can be unreliable; this concern has been voiced since the early 1900s and has prompted efforts to secure energy from domestic sources instead. And finally, reliance on fossil fuels is unsustainable because the supply is finite and someday it will simply run out.

All of these factors have pushed scientists to pursue alternative energy sources, such as wind and sun. Slowly but surely, these alternatives are replacing fossil fuels in our electricity supply, but when it comes to cars, trucks, and airplanes, fossil fuels are still at the forefront. Electric and hybrid cars

are available, but because trillions of dollars are currently invested in fossil-fuel-specific vehicles and infrastructure, finding liquid fuels that can be dropped directly into this system will create the most immediate improvement.

Biofuels have long been touted as a potential solution. However, biofuel production is challenged both by the ability to grow enough plants (biomass) that are not otherwise needed as food and by the ability to efficiently process that biomass into a fuel that is competitively priced, energy dense, and versatile enough to be used for various types of vehicles and conditions.

Scientists at Los Alamos are tackling this challenge from many angles—from increasing the growth of plants and algae to developing strategies to convert biomass into fuel and other useful chemicals. This latter task, converting biomass, is significant because harvesting hydrocarbons from contemporary plants is not as easy as it is from fossilized ones, and once harvested, they are not anything like crude oil. Fortunately, a handful of Los Alamos chemists have been studying the process and are closing in on a strategy to condense millions of years of fossilization into a few chemical reactions—thus removing Father Time from the equation completely.

Taking the bio out of biofuels

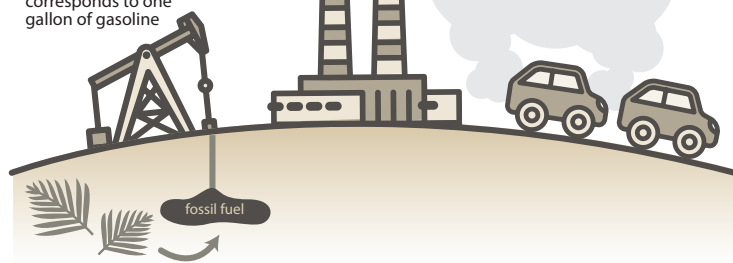
Chemist Andrew Sutton came to Los Alamos as a postdoctoral fellow to work on hydrogen storage for energy research. But when his mentor, Lab chemist John Gordon, began to investigate biomass conversion as a new direction for energy improvements, Sutton—now a staff scientist—became engaged as well. Their goal: to use chemistry to construct gasoline-like hydrocarbons from plant sugars. This approach deviates from traditional, long-standing biological methods of using microbes to convert plant sugars into alcohol fuels.

FOSSIL FUEL PROCESS

196,000 lbs of prehistoric plant matter (containing CO₂ from the ancient atmosphere) corresponds to one gallon of gasoline

5 lbs CO₂ emissions per gallon of gasoline for extraction, processing, and transportation

19 lbs CO₂ emissions per gallon of gasoline from combustion



BIOFUEL PROCESS

Biofuel crops consume atmospheric CO₂ as they grow

Emissions from biofuels processing

Emissions from combustion are offset by the CO₂ absorbed by biofuel crops



Biofuels are desirable as alternatives to fossil fuels because instead of releasing previously buried carbon into the atmosphere, the carbon dioxide released comes from plants that actively removed it from the atmosphere during their growth. The downsides to biofuels are mostly associated with the energy and resources required to grow the plants and process the fuel. Chemical conversion of plant sugars to third- and fourth-generation hydrocarbon biofuels has the potential to significantly reduce this energy input and cut greenhouse gas emissions by 80 percent compared to fossil fuels. SOURCES: Jeffrey Dukes in *Climate Change*, Union of Concerned Scientists

Alcohol-based fuels such as ethanol were used in many of the first car engines. In 1925, Henry Ford was quoted in *The New York Times* as saying, “There is fuel in every bit of vegetable matter that can be fermented. There’s enough alcohol in one year’s yield of an acre of potatoes to drive the machinery necessary to cultivate the fields for a hundred years.”

Today, ethanol fuel—a so-called first-generation biofuel—is made from sugars found in corn and sugarcane. Plant biomass is mostly made of sugars, which are rings of five or six carbon atoms connected to many oxygen atoms. Multiple sugars linked together make carbohydrates, which provide fuels for living creatures large and small. Humans and other animals convert them into energy, water, and carbon dioxide, while some microbes, such as yeast and bacteria, use a fermentation process to convert them into carbon dioxide and an alcohol, such as ethanol.

The carbohydrates in corn kernels and cane sugars are easy to access for fuel production. However, corn and sugar are food crops that will increase in price if a portion of the supply is also being used to power cars. To address this, researchers have been improving ethanol production from other, less valuable plant parts such as non-edible leaves and stalks, or from non-food plants such as grasses. This production, however, is more difficult because leaves, stalks, and grasses have evolved to be strong and stable, and their sugars are trapped in a complex molecular structure. The carbohydrate building blocks are locked together within a polymer called cellulose, which is then wrapped up with another polymer called lignin.

Through a lot of hard work, scientists have been successful in deconstructing this lignocellulose into its carbohydrate building blocks so that microbes can ferment them into ethanol fuel. Unfortunately, this second-generation fuel, dubbed cellulosic ethanol, is still not a complete replacement for traditional gasoline because the fermentation process releases carbon dioxide, which both increases the overall carbon footprint of ethanol as a fuel, and decreases its energy density.

“Ethanol’s benefits are limited,” says Pete Silks, a chemist at Los Alamos who has worked on biomass conversion for many years. “It is corrosive, and it is not as energy dense as

gasoline. Also, it freezes at low temperatures so it can’t be used as aviation fuel.” Furthermore, because most people don’t drive ethanol-ready vehicles, the only way to have widely useable biofuels in the near term is to create gasoline and diesel, instead of ethanol, from plants.

But how? The current process of making ethanol relies on microorganisms that convert five-carbon sugars into two-carbon ethanol. Gasoline and diesel fuels are made of hydrocarbons that have many more carbon atoms, fewer oxygen atoms, and fewer double bonds. So, unless someone discovers a new organism that digests sugar directly into gasoline, scientists are challenged to remove oxygen atoms, break double bonds, and extend carbon chains—as would naturally happen during the eons-long fossilization process—in the confines of a chemistry lab.

The language of fuel

Traditional petroleum-based fuels are made of a mixture of different types of hydrocarbon molecules, and getting the right mixture is critical. Gasoline, for instance, can contain molecules that range from 5 to 13 carbon atoms in length. Diesel hydrocarbons range from 10 to 25 and jet fuel from 9 to 13. Some of the molecules contain double bonds between carbon atoms, while others don’t. Some contain rings of carbon, while others are linear. And although carbon and hydrogen are the dominant elements in fuels, there are sometimes a few oxygen molecules present as well.

To improve their fuel-development research, Sutton and his Los Alamos colleagues have been able to fine-tune their approach by collaborating closely with fuel engineers—despite it seeming, at first anyway, that they were speaking entirely different languages! For example, chemists often think about which atoms are connected to what, so to them, the term “octane” describes an eight-carbon molecule with many hydrogen atoms. However, fuel engineers tend to focus on the properties of a molecule; in that context, octane is an indicator of performance. High-octane fuel might contain a large number of eight-carbon molecules, but to a fuel engineer, it generally

conjures up discussion of how much the fuel-air mixture can be compressed without causing engine damage.

Through this collaboration, the Los Alamos chemists began to map fuel-related characteristics—viscosity, flash point, and volatility—to various types of molecules available from biomass, such as those with a carbon atom double bonded to an oxygen atom (ketones) and those containing carbon rings

WE ARE CONDENSING MILLIONS OF YEARS OF FOSSILIZATION INTO A FEW CHEMICAL REACTIONS.

(cycloalkanes). Their most recent paper describes many of these relationships, including how the length of a carbon chain affects the density of a fuel and what happens to the boiling point if there are any double bonds within the molecule. This analysis has helped the scientists realize, for instance, that they did not actually have to remove all the oxygen atoms from the sugars, as they had previously thought. Instead they should be strategic about which types of oxygen-containing molecules to retain and where they should be located.

Coaxing carbons to cooperate

In a cellulosic ethanol production line, the fuel conversion happens toward the end. Biofuel crops must first be grown, harvested, and preprocessed to break apart the lignocellulose structure. Some methods use extreme temperatures and pressures to unlock the structure and release the chemical building blocks. Another method of processing essentially cooks the biomass in water, acid, and cellulose-breaking enzymes. The result is a brown, mucky-looking liquid called hydrolysate that contains mostly glucose and xylose sugars. The hydrolysate sugars can then be fed to microbes that will convert them into fuel.

This is where Sutton and his colleagues step in. Instead of sending the hydrolysate to a bioreactor for microbes to ferment into ethanol, their chemistry-based approach uses regular, off-the-shelf chemicals under mild conditions to create hydrocarbon fuels.

In order to convert five- and six-carbon sugars into gasoline, the chemists must first add carbon atoms to make longer carbon chains that more closely resemble fuel hydrocarbons. This reaction uses a catalyst (a molecule that can

speed up the reaction without itself getting used up) to take a six-carbon sugar and a simple three-carbon molecule, such as acetone, to make a nine-carbon molecule. Other variations can create a range of 8 to 16 carbon atoms.

After elongating the carbon chain, the Los Alamos scientists break apart the rings and remove some of the oxygen atoms. They had to experiment with various ways of opening

the ring first, because removing the oxygen first would make the ring more stable and therefore harder to break. For this, they

developed a novel protocol that uses acid, hydrogen gas, and palladium as a catalyst to successfully transform the molecules while keeping energy input at a minimum.

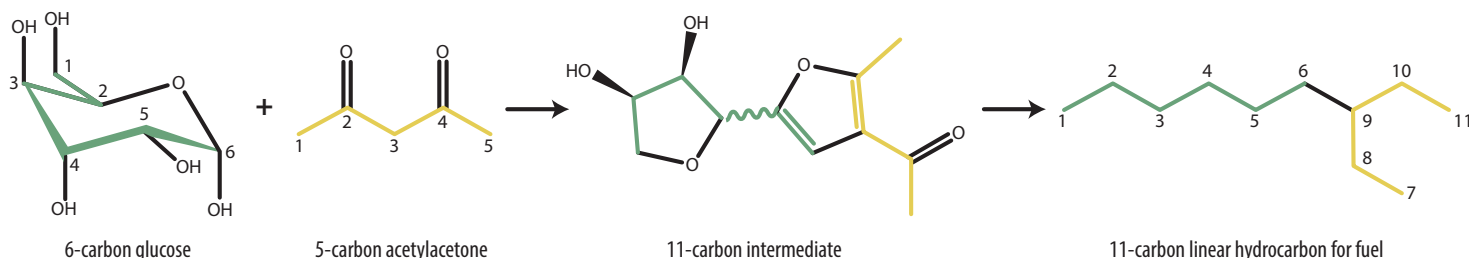
The team has refined these protocols using various starting materials, including sugar, a sugar derivative called 5-hydroxymethylfurfural, and a potato. Then they tried their methods on hydrolysate and were able to demonstrate feasibility for an industrial production environment.

Once these basic steps had been mastered, Sutton and his colleagues began to experiment with various ways of improving the sugar-to-fuel conversion to make it even more efficient and less expensive. These modifications are critical for making biofuels cost-competitive.

The big time

Global transportation infrastructure is designed for fossil fuels, and traditional gasoline is currently much less expensive than biofuels. Every approach to biofuel production is faced with this reality, pushing scientists to examine each step of the process to find improvements. Some of the comparatively high costs and high emissions of biofuel production lie in the growing, harvesting, and preprocessing of biomass. However, in looking at their conversion protocol, Sutton and his team were able to identify a number of additional changes they could make that may further help.

“By keeping temperatures relatively low and pressures close to normal, we can do these reactions in distributed facilities. In other words, we don’t have to transport all the biomass to large biorefineries,” says Sutton. Transporting such biomass—which is heavy because it is full of water—not only adds cost but also increases its carbon footprint.



An example of chemical conversion wherein a six-carbon glucose molecule is combined with a five-carbon acetylacetone molecule. The final product is an 11-carbon hydrocarbon fuel molecule, similar to those found in crude oil, color coded above to indicate where its carbon atoms originated. (As is customary in organic chemistry, each vertex or endpoint not otherwise labeled is assumed to be a carbon atom, plus any hydrogen atoms needed to occupy the carbon bonding sites not already specified in the drawing.)

CATALYZING A NEW ECONOMY

Three-quarters of the volume of U.S. crude oil is used to make fuel, with revenues totaling \$935 billion. A mere 16 percent goes toward chemicals for consumer products yet still generates comparable revenues of \$812 billion. Such petrochemicals are everywhere—they are used to make

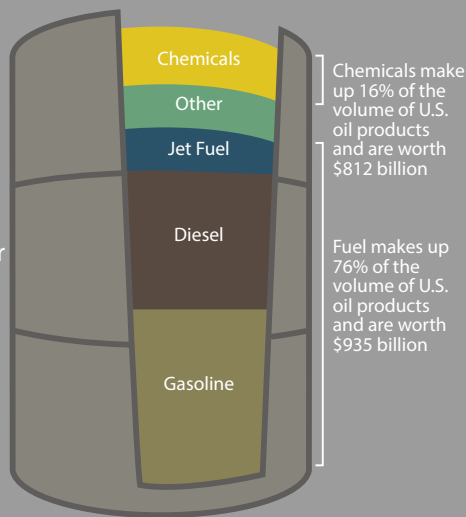
solvents, plastics, waxes, detergents, pharmaceuticals, and even artificial flavors. When it comes to making competitively priced biofuels, researchers would like to offset the biofuel production cost by supplying comparably profitable bio-derived chemicals in place of the petroleum ones.

Los Alamos chemists Pavel Dub and John Gordon spent the last few years studying how molecular catalysts work, and what they've learned could greatly improve the prospects for creating commodity chemicals from biomass. In 2001, the Nobel Prize in Chemistry was jointly awarded to three chemists, including Ryoji Noyori, who discovered a very efficient molecular catalyst for adding hydrogen atoms (hydrogenation) to molecules that contain carbon-oxygen double bonds. The catalyst contains a metal center bound to several different molecules called ligands. In this particular type of catalyst, one of the ligands contains a nitrogen atom bonded to a hydrogen atom. The efficacy of this catalyst is linked to the N-H group; it was believed that this N-H functionality facilitates the reaction by transferring a hydrogen atom.

Recent work by Dub and Gordon challenges this idea, suggesting instead that the ligand really facilitates the catalytic reaction by holding the hydrogen atom in a strong hydrogen bond interaction rather than transferring it.

"The strength of this hydrogen bonding interaction, or its absence, determines whether or not the N-H functionality is even necessary," says Gordon. Through this work, he and Dub discovered a new class of catalysts without the N-H functionality, the activity of which is comparable to Noyori-type catalysts.

How will this help create greener shampoos and plastics? Most of the biomass-derived chemicals that could be made into commodity items include carbon-oxygen double bonds that need to be hydrogenated. This hydrogenation could be done using the new catalysts in small amounts, under mild conditions, at low cost, and with operational simplicity, which raises the possibility that the new catalysts could be used on a petrochemical scale. Since scientists are looking for all possible routes to replace the entire barrel of crude oil with plant matter, this discovery could truly be a catalyst for change.



Troy Semelsberger (left) and Andrew Sutton stand alongside the continuous flow reactor developed by their team. This high-throughput environment stands to improve biofuels production by enabling more efficient chemical conversion of biomass into hydrocarbon fuels.

The team also determined that the catalyst palladium, which costs about \$30 per gram, could be replaced with a type of nickel that only costs \$0.08 per gram. And to address the large costs incurred separating catalysts and reagents from reactants at various steps of the process, Sutton's team found ways to streamline everything by changing some of the chemicals used—such as eliminating corrosive acids—so the separations would no longer be necessary.

A less expensive conversion process is definitely a step in the right direction, but another problem is scaling; in order to produce billions of gallons of fuel, scientists need to demonstrate how to convert biomass on a very large scale. To tackle this, Sutton and his team enlisted the help of Los Alamos engineers Bill Kubic and Troy Semelsberger to create a continuous flow reactor in which the chemical conversion could take place in a high-throughput environment more conducive to producing large amounts of fuel at a time. The flow reactor also allows the chemicals to be in constant contact with the catalysts, thus increasing efficiency.

Altogether, these improvements are advancing next-generation bio-gasoline, biodiesel, and bio-aviation fuel. Although Sutton doesn't expect cars to be running on 100 percent biofuel anytime soon, he knows it won't be long before they are using a blended combination of fuels—ethanol, bio-gasoline, and regular petrol. Making more hydrocarbon fuels from biomass would not only be good for the planet, but would also allow existing infrastructure to be used and not go to waste—meaning people could go green without having to buy a new car. And that means leaving more of Father Time's legacy untouched, which would surely make Mother Nature proud.

—Rebecca McDonald

More biofuels research at Los Alamos

- **Advances in algal biofuels research**
<http://www.lanl.gov/discover/publications/1663/issues-archive/january2012.pdf>
- **Genomics for identifying candidate fuels**
<http://www.lanl.gov/discover/news-stories-archive/2016/February/acids-from-algae.php>
- **Improving photosynthesis to increase yield for fuels and food**
<http://www.lanl.gov/discover/news-release-archive/2015/December/12.03-frontiers-in-science.php>

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